

Electronic Structure of the YH_3 Phase from Angle-Resolved Photoemission Spectroscopy

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Yttrium can be loaded with hydrogen up to high concentrations causing dramatic structural and electronic changes of the host lattice. We report on angle-resolved photoemission experiments of the Y trihydride phase. Most importantly, we find the absence of metal d -bands at the Fermi level and a set of flat, H -induced bands located at much higher binding energy than predicted, indicating an increased electron affinity at H sites.

73.61.-r, 71.20.-b, 79.60.-i, 71.30.+h, 71.20Eh

Recently, switchable optical properties of metal hydrides at ambient pressures and temperatures have attracted strong interest. [1] For trivalent Y , for instance, up to three hydrogen atoms can be absorbed. The dihydride is even a better metal than Y itself but during the transition to the trihydride phase it turns from shiny metallic to transparent and insulating. With hydrogen a proton and an electron are introduced to the metal host. This results in doping the host material. Different models have been proposed to explain this spectacular metal-insulator transition. However, the behavior of H in such hydrides is still under debate.

State-of-the-art *ab-initio* local density approximation (LDA) calculations do not reproduce the optical gap necessary to explain the transparent state in the trihydride phase unless additional symmetry lowering is considered by displacing H atoms away from positions given by the HoD_3 structure of YH_3 . [2]

Other models [3,4], based on strong electron correlations, have been proposed to explain the metal insulator transition. Ng et al. [3] studied the effect of correlations on the bandwidth of hydrogen induced states. Hydrogen is present in the form of H^- as determined from electromigration experiments [5], where one electron is taken from the metal host. The two electrons on H^- are strongly correlated and the essence of the result of Ng et al. [3] is that the opening of the band gap is due to a correlation-induced band narrowing.

The model of Eder et al. [4] is based on the observation that the radius of the hydrogen is very sensitive to the occupation number. The two electrons on H^- are correlated but with drastically different radii around the proton. This results in a so-called breathing mode and a local singlet-like bound state with one electron on the proton and the other on the neighboring metal orbitals. Already at the meanfield level this introduces a significant correction to the potential at the H site, effectively increasing the electron affinity, lowering the hydrogen band and opening the gap. There is an interesting and appealing connection between this model and the Zhang-Rice singlet [6] in high temperature superconductors (HTc's). The two electrons form a singlet analogous

to holes in the HTc's.

On the other hand, very recent so-called GW-calculations [7,8] demonstrate the formation of a sufficient gap to explain the metal-insulator transition without need of strong electron correlations. Rather, these calculations indicate that the gap opening is described as in normal semiconductors. For semiconductors LDA does not produce the correct gap whereas the self-energy corrections included in the GW-calculations are able to account for this deficiency.

Indeed, detailed angle-resolved photoemission (ARPES) experiments are needed to favor one or the other model. However, practically all previous work on metal hydrides has been done on polycrystals and/or on samples that are capped with a protective Pd layer. In order to perform ARPES experiments, uncapped single crystalline material is needed. Furthermore, preparation has to take place *in situ* since Y is extremely reactive.

Here we present, to our knowledge, the first ARPES data on the trihydride phase of uncapped single crystalline films. We find that the overall bandwidth of the Y trihydride phase agrees with LDA calculations. However, a set of flat bands is observed with significantly higher binding energy, a fact that argues in favor of ideas of the model proposed by Eder et al. [4].

Experiments were performed in a Vacuum Generators ESCALAB Mk II spectrometer with motorized sequential angle-scanning data acquisition. [9] ARPES measurements were performed with monochromatized He I α ($h\nu = 21.2$ eV). The setup including a plasma discharge lamp with monochromator is described elsewhere [10]. The energy resolution is 35 meV for He I α measurements. All measurements have been done with the sample kept at room temperature. The substrate used to grow on the single crystalline Y hydride films was a W(110) single crystal. Details of the set-up used, the preparation and the careful characterization of the crystal and electronic structure and the calibration of the H -concentration has been described elsewhere [11,12]. In brief, this set-up allows to prepare clean, single-crystalline rare-earth hydride films using hydrogen pressures up to 1.3 bar. It combines a high-pressure reaction cell with a custom

made hydrogen purification system based on a Pd-24%Ag permeation tube and a sorption pump, i.e., a getter alloy (70%Zr-24.6%V-5.4%Fe). The hydrogen purification system removes residual contaminations from 6N H_2 gas efficiently. The overall design is such that the sample never gets in contact with non ultra-high-vacuum compartments. The results presented here are taken from 200 Å thick, well-ordered single crystalline films [11] in the trihydride phase. The hydrogen composition is determined via photoelectron diffraction and X-ray photoelectron spectroscopy (not shown) to be $YH_{2.9}$. [11]

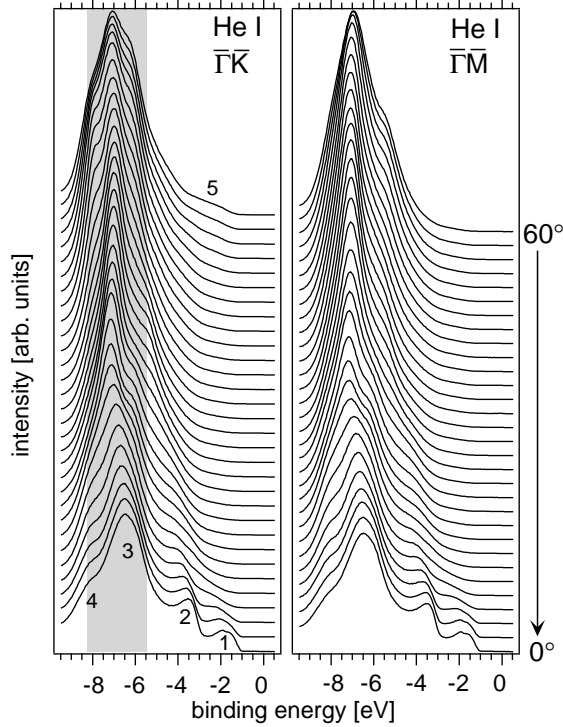


FIG. 1. Energy distribution curves taken along the $\bar{\Gamma}\bar{K}$ (left) and $\bar{\Gamma}\bar{M}$ (right) directions of the surface Brillouin zone (see Fig. 2) using HeI ($h\nu = 21.2$ eV) radiation and collecting spectra up to 60° off-normal emission. Normal emission (0°) corresponds to $\bar{\Gamma}$; the \bar{K} and \bar{M} points are reached approximately at 17° and 15° off-normal emission, respectively, for 0 eV binding energy. Mapping into k-space is shown in Fig. 4. A shaded area marks weakly dispersing, broad spectral features (see text).

Bandstructure calculations using the full-potential linearized augmented plane-wave method [13] within the generalized-gradient approximation [14] have been performed for comparison with the experiments. Calculations were performed for the HoD_3 structure with space group 165 ($P\bar{3}c1$). The lattice parameters used for the YH_3 calculation were $a = b = 6.34$ Å and $c = 6.6$ Å. A total of 485 k-points within the irreducible wedge of the Brillouin zone (BZ) were considered for the self consistency cycles and convergence was reached to within 0.1 mRy.

Figure 1 shows ARPES data measured along two high symmetry directions of the surface BZ. The situation in reciprocal space is illustrated in Fig. 2 where the surface BZ (left) and a cut through the extended bulk Brillouin zone containing the Γ, A, H, L, M, K high symmetry points (right) is shown. YH_3 with the HoD_3 structure consists of a $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ reconstruction with respect to the hexagonal Y-lattice, i.e., the unit cell has a and b vectors which are $\sqrt{3}$ times longer and rotated by 30° . Therefore the YH_3 BZ is smaller and rotated accordingly (Fig. 2).

Inspecting the experimental spectra (Fig. 1) a similar behavior is observed for both directions. The dispersion appears relatively weak and the electronic states do not reach the Fermi level (E_F) or 0eV binding energy, which is indicative for a gap. The d -states that are present in Y ($[Kr]4d^15s^2$) and YH_2 (not shown) have disappeared. [15] Five dispersing features are easily discernible and are labeled from 1 to 5. A broad almost dispersionless maximum between 5.5 and 8.3 eV (shaded area) persists for all angles respectively k -points. At first sight one is tempted to interpret the fact that the dispersion is weak and the spectral features are broad as caused by strong electron correlations and self-energy effects.

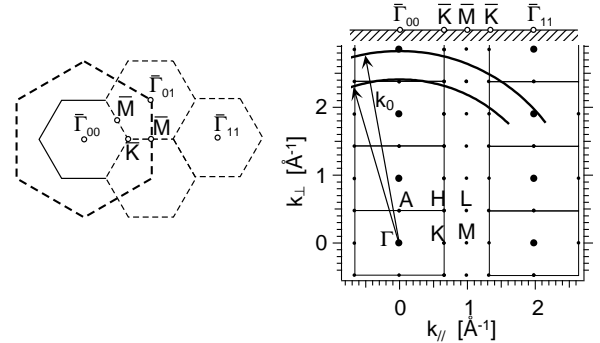


FIG. 2. Situation in k-space. (Left) The surface Brillouin zone for the HoD_3 structure with high symmetry points. The large hexagon represents the surface Brillouin zone for the Y sublattice. (Right) Section across the bulk Brillouin zone containing the Γ, A, H, L, M, K high symmetry points. Spherical segments indicate the k-space region probed within the free-electron final state approximation used for the model calculation in Fig. 4.

However, taking a closer look reveals a different point of view. In Fig. 3 the result of our bandstructure calculation of YH_3 in the HoD_3 structure is displayed. As mentioned above the approach using LDA does not show a gap and the system is metallic. The calculation presented here is in good agreement with the published results of Kelly et al. [2]. We notice that there are many bands. This is a consequence of the large real-space unit cell of the HoD_3 structure containing many atoms. In fact, there are 24 atoms including 6 yttrium atoms and 18 hydrogen atoms in the unit cell. The important point to

notice here is that there is a set of rather flat, hydrogen-induced bands (as deduced from a band character analysis) between 1.8 and 4.6 eV (dark shaded area) extending over the whole bulk BZ. Such a set of flat bands naturally gives rise to a high density of states in this energy region and leads to the interpretation of the broad, high intensity features in the experiment (shaded area in Fig. 1) in terms of these flat bands. The energy width of the region in the experiment agrees well with the energy interval of the flat bands in the bandstructure calculation. The only difference is that the experimental bands occur at a 3.7 eV greater binding energy.

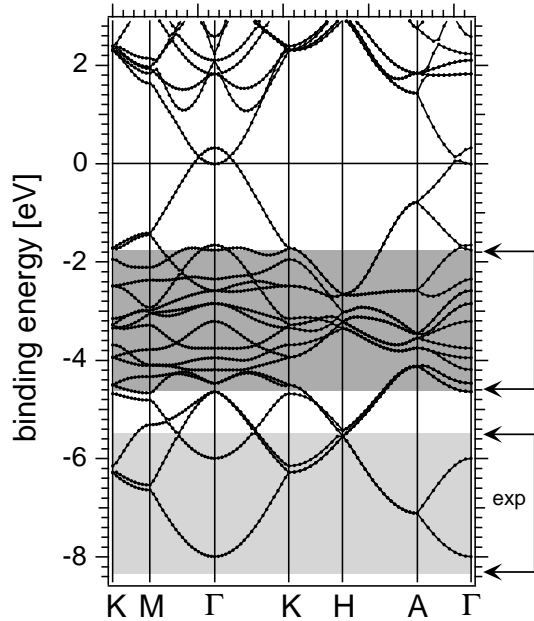


FIG. 3. LDA based bandstructure calculation for the HoD_3 structure. Indicated is the region (dark shading) of flat, hydrogen-induced bands and the corresponding region (light shading) where the experiment (Fig. 1) shows a high density of states. (see text)

In order to obtain a more detailed comparison we use a gray scale representation of both, the experimental data and the calculated band structure. Figure 4 displays the results along the $\bar{\Gamma}\bar{K}$ -direction. For the experimental data (left) the second derivative of the spectra of Fig. 1 have been plotted as a function of the wave vector parallel to the surface. The reason for plotting the second derivative is to flatten the spectra and to accentuate the dispersing features. The calculation (right) follows the free electron final state wave vectors drawn in Fig. 2 [16]. Again we can identify the flat bands (marked by shading the energy scales) in both the experiment and the calculation where they occur with a 3.7 eV smaller binding energy. In addition we can identify the bands labeled 1 to 5 as already indicated in Fig. 1. Therefore comparing our experiments with the LDA calculation shows that the overall band width compares well. The differences are a

rigid shift of approximately 1.5 eV and the position of the flat bands. However, a detailed comparison of different bands and their relative positions depends on the validity of the free-electron final-state approximation. Therefore we cannot, at present, give a robust statement about the exact position of the top of valence band (label 1, Fig. 4, left) and, as a consequence, about the size of the gap. This depends on the exact location in the component of the wave vector perpendicular to the surface, k_{\perp} . On the other hand, the difference in the position of the flat bands is independent of this approximation since the flat bands extend over the whole BZ as seen from experiment (Fig. 1) and theory (Fig. 3).

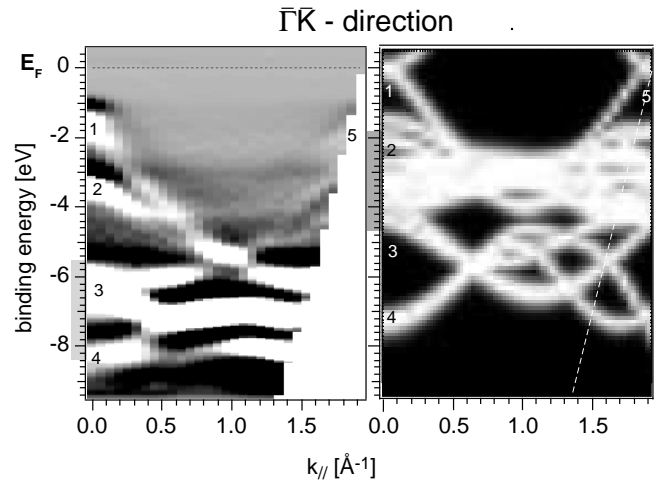


FIG. 4. Second derivative of spectra from Fig. 1 mapped into k -space using gray scale intensity coding with high intensity in white (left). Model calculation using the free electron final state approximation (right) (see text).

It is interesting now to compare our results with theoretical models. At first we look at the GW calculations. In the study of Miyake et al. [7] the gap opens due to a shifting up of the conduction bands whereas in the case of van Gelderen et al. [8] the gap opens because of both, shifting up of the conduction bands and shifting down of valence bands. Otherwise the quasiparticle wavefunctions are practically identical to the LDA wave functions and there is basically a one to one correspondence between the bands of the LDA and GW bandstructures. The total band widths do not differ significantly as well. From our experiments we conclude that the overall bandwidth is well reproduced by LDA and GW-calculations. However, the high binding energy of the flat bands is not reproduced. Even the downwards shift of the valence bands (≈ 1 eV) in the case of van Gelderen et al. [8] is not sufficient and does not account for the *relative* shift of certain bands. Nevertheless, from the comparison in Fig. 4 (therefore assuming the free-electron final-state to be valid) we notice that a downward shift of the LDA results, as would be obtained for the GW-calculation pro-

duces quite a good agreement if we do not consider the flat bands.

Clearly, the good agreement of the overall bandwidth with the LDA calculations is in contrast to the model of Ng et al. [3] where strong electron correlations induce a band narrowing. However, we cannot exclude that individual bands are subject to significant narrowing. The reason is that from the experimental data, basically due to the large number of bands, it is not possible to identify every individual band. The width of the experimentally observed spectral features is not resolution limited and might be explained either by self-energy effects or also by a relatively high mobility of hydrogen atoms and defects due to the substoichiometry of the films. Furthermore, there is still debate on whether the HoD_3 structure really corresponds to the one for YH_3 . [17,18]

Finally we compare our results to the model by Eder et al. [4]. The dependence of the occupation number of electrons on the hydrogen site is incorporated in their model Hamiltonian by having a novel hopping integral. The resulting singlet-like bound state is manifest via increasing the binding energy of the hydrogen states. This model and the one by Ng et al. [3] have in common that they treat hydrogen as impurities in the background of the metal atoms. However, whereas in the treatment of Ng et al. the result is a narrowing of bands, Eder et al. [4] predict a shift of the potential at the hydrogen site *retaining* the broad hydrogen band.

It is now very tempting to interpret our data, showing a shift of bands towards higher binding energy, in terms of such an additional potential on hydrogen sites. Observing Fig. 3 it appears that only the set of flat bands is strongly shifted down whereas the others, covering the full bandwidth, are consistent with the GW approach. This might be interpreted in the sense that the bands within the set of flat bands have a more localized character and therefore are stronger affected by the singlet-like bound state. However, a detailed comparison of how different bands are affected is not possible since a realistic bandstructure for the HoD_3 structure is not available within Eder's model Hamiltonian.

In conclusion we have performed ARPES experiments on single crystalline films of Y in the trihydride phase. A comparison with LDA calculations shows a good agreement of the overall bandwidth. No significant band narrowing is observed although a narrowing of individual bands cannot be excluded. However a set of hydrogen induced, flat bands are identified in the experiment with a binding energy ≈ 3.7 eV higher than in the calculation. Furthermore, based on the free-electron final-state

approximation, we infer a rigid shift of the valence band towards higher binding energy by more than 1 eV which is consistent with GW-calculations [8] and the opening of a gap. The downwards shift of flat bands supports the model proposed by Eder et al. [4] predicting a shift of the potential at the hydrogen site and *retaining* the broad hydrogen band.

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